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Neutron diffraction study of Ti substituted Ni-Zn ferrites

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Abstract : Neutron diffraction and magnetic measurements have been carried out to understand the magnetic behaviour of titanium substituted Ni-Zn ferrites. The net magnetic moment (μ_B) and Curie temperature (T_c) decrease with increase in titanium content. The experimental values of magnetic moment obtained from neutron diffraction and magnetic measurements are found to be less than those calculated with Neel's model. Gilleo's model has also been used to calculate T_c values. It is concluded that canted spin arrangement is favoured in these ferrites.

Keywords : Ferrites, magnetic structure, neutron diffraction

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1. Introduction

Nickel ferrites with proper substitution are widely used as magnetic materials due their high electrical resistivity, low eddy currents and dielectric losses. These materials are extensively used in magnetic recording media, computer memory chips, microwave devices *etc*. The investigation of cation distribution and oxygen positional parameters '*u*' provides a mean to develop materials with desired properties which are useful in industry. Extensive work has been done by various workers to upgrade the properties of ferrites by substituting different types and amounts of impurities. It has been reported [1–3] that by the addition of small amount of tetravalent ions like titanium or tin, the electrical and magnetic properties of basic Ni-Zn and Mg-Zn ferrites can be significantly altered. It is well known that neutron diffraction study offers several

advantages in the determination of magnetic properties of spinel ferrites. The marked difference in nuclear scattering amplitude of the cations and interaction of their magnetic moment with the neutron magnetic moment makes possible the accurate determination of cation distribution and magnetic structure.

In order to understand the cation distribution and its effect on the magnetization behaviour, we have carried out neutron diffraction, low field a.c. susceptibility and magnetization measurements on titanium substituted Ni-Zn ferrites.

2. Experimental

The samples of the series $Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O_4$ (with x = 0.2, 0.4 and 0.5) were prepared by ceramic method. AR grade NiO, ZnO, TiO_2, Fe_2O_3 were weighed in required proportions and mixed thoroughly. These powders were pre-sintered in air at 800°C for 10 hours. The pellets were made and finally sintered at 1100°C for 24 hours in air and then slowly cooled. The formation of single phase was confirmed by X-ray diffraction. Magnetization measurements were carried out on high field loop tracer. A.c. susceptibility (χ_{ac}) was measured using low field a.c. susceptibility technique, and Curie temperature was obtained from the normalized susceptibility *vs* temperature plots.

Neutron diffraction measurements were carried out on polycrystalline samples using the position sensitive detector based powder diffractometer at Dhruva reactor at BARC. Monochromatic neutrons having wavelength of 1.094 Å were used for the experiment. The samples were packed in cylindrical vanadium container. Diffraction profiles were recorded at 300 K in the angular range 20° to 100°. The patterns showed single phase compounds. The data were analyzed using Rietveld profile refinement technique for both chemical and magnetic structure [4,5].

3. Results and discussion

These compounds are magnetically ordered at 300 K. Therefore, only higher angle data, where the magnetic contribution to the Bragg peak is negligible, were first refined to get the chemical structure [6]. For the system under study, the occupancies of some of cations were fixed considering their site preference. It is well known that Zn has strong preference for *A*-site and Ni has strong preference for *B*-site. In the refinement therefore, all the Zn ions were put on the *A*-site, and all Ni ions on *B*-site. The oxygen position parameter (u) was varied in addition to profile half width parameters. The site occupancies of Fe and Ti were varied independently. The fitted and observed profile for the compositions x = 0.2 is shown in Figure 1, along with the difference plot.

The results of the refinement are summarized in Table 1. It is observed that the lattice parameter a and the oxygen position parameter (u) were found to be almost constant. From cation distribution it is observed that titanium occupies both the sites.

The *A*-site magnetic moment was deduced from the intensities of (220) and (422) reflections. The structure factors of both these reflections have contribution from *A*- site

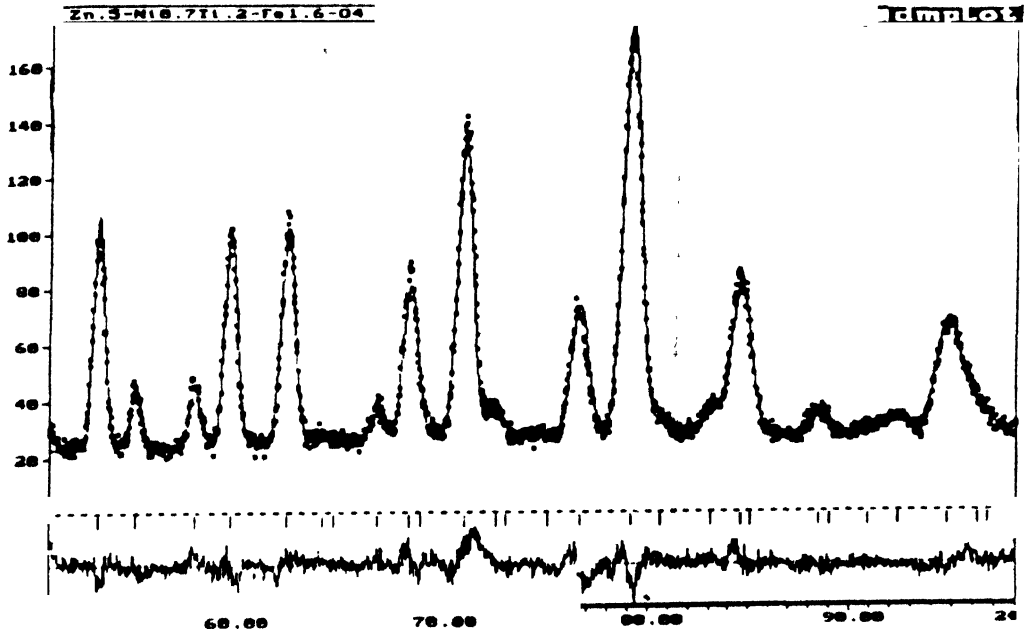

Figure 1. Profile fitted Neutron diffraction pattern for $Ni_{0.7}Zn_{0.5}Ti_{0.2}Fe_{1.6}O_4$ along with difference plot.

Table 1. Parameters obtained from Rietveld profile refinement, for $Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O_4$ system.

Parameter	Content of x		
	0.2	0.4	0.5
Lattice constant a (Å)	8.4016	8.3916	8.4090
Oxygen parameter u (Å)	0.2568	0.2569	0.2572
Temperature factor B (cm^2)	0.48	0.35	0.34
Cation distribution	$(Zn_{0.5}Ti_{0.08}Fe_{0.42})$ $[Ni_{0.7}Ti_{0.12}Fe_{1.18}]$	$(Zn_{0.5}Ti_{0.12}Fe_{0.38})$ $[Ni_{0.9}Ti_{0.28}Fe_{0.82}]$	$(Zn_{0.5}Ti_{0.16}Fe_{0.34})$ $[Ni_{1.0}Ti_{0.34}Fe_{0.66}]$
b_A	0.6582	0.6969	0.5539
b_B	0.9036	0.8084	0.7720
R_p	5.29	5.91	5.57
R_{wp}	6.73	7.52	7.10
R_{exp}	4.84	5.83	5.03
R_B	5.72	6.49	6.95

Table 1. *(Cont'd.)*.

Parameter	Content of x		
	0.2	0.4	0.5
	From magnetic structure analysis		
μ_A	1.26(6)	1.21(8)	1.25(5) 1.29 at 12 K
Free ion	1.53	1.33	1.17
μ_B	1.74(8)	1.31(5)	0.41(8) 49 at 12 K
Free ion	2.66	2.06	1.83

magnetic moment only. The B-site moment was obtained using (222) reflection, the intensity of which depends on B-site magnetic moment.

These values were used as initial parameters for magnetic profile refinement. The values obtained after refinement are almost same as those derived from the intensities. The fitted profile with magnetic reflections for one of the compositions $x = 0.2$ is shown in Figure 2. The values of magnetic moments obtained as given in Table 2. The magnetic

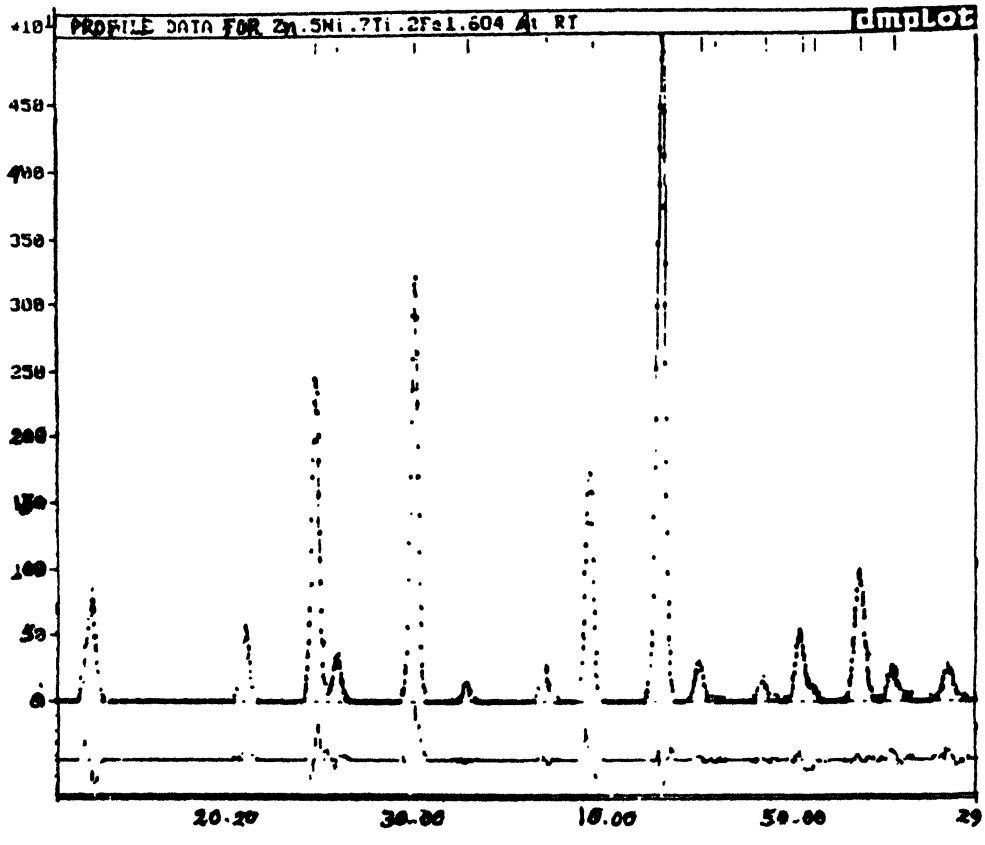

Figure 2. Profile fitted pattern with magnetic reflections for $Ni_{0.7}Zn_{0.5}Ti_{0.2}Fe_{1.5}O_4$ along with difference plot.

moment (μ_B) determined from hysteresis and from neutron study for different values of x are given in Table 2. These values are in good agreement with each other, the μ_B value decreases with increase in x.

Table 2. Magnetic moment and Curie temperature from various methods for $Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O_4$ system.

Content	Magnetic moment (μ_B)			Curie temperature (K)	
n	From neutron	From magnetic measurement	From Neel's model	From suscep-tibility	From Gilleo's model
0.2	2.22	2.52	5 22	535	478
0 4	1 41	1 69	4	475	422
0.5	0.43	1.05	3.54	460	385

The magnetization behaviour in ferrites is explained on the basis of Neel's molecular field model. Considering the magnetic ions on both tetrahedral (A) and octahedral (B) sites, the possible exchange interactions are the two intrasite (AA and BB) and one intersite (AB). Amongst the three magnetic interactions in intersite AB interaction in the strongest one. In this model, collinear arrangement of magnetic moments of individual site are presumed, *i.e.* the magnetic ions on each sublattice are ferromagnetically aligned with an opposite alignment of intersite moments. The net magnetization is the vector sum of the octahedral (B) and tetrahedral (A) site magnetization. The μ_B values are calculated using Neel's two sublattice model with suitable correction for the Brillouin's function and using the cations distribution obtained from neutron diffraction. These values are given in Table 2. The μ_B values show a decreasing trend with x. However, the theoretical μ_B values are higher than the experimental values indicating a deviation from the collinear arrangement of moments.

Gilleo's model :

The magnetic moment and Curie temperature were calculated using the Gilleo's model [7,8]. With the assumption that magnetic moment actively participate in ferrimagnetism only when it interacts with two or more magnetic ions in different coordination. Gilleo has proposed a statistical model which neglects intrasublattice interaction and thus no canted spin is considered.

According to this model the Curie temperature is proportional to the number of active linkages per magnetic ion per formula unit and is given by

$$T_c(K_o, K_t) = (3/24) \times \left[\{n(K_o, K_t)\}/\{24(N(K_o, K_t))\}\right] \times [T_o(0, 0)].$$

Here, $T_o(0, 0)$ – Curie temperature of unsubstituted ferrite,

$n(K_o, K_t)$ – active magnetic interaction per formula unit,

$N(K_o, K_t)$ – the number of magnetic ions actively participating in the ferrimagnetisation,

K_o, K_t – the fraction of ions substituted on octahedral (B) and tetrahedral (A) sites, respectively.

24/3 – number of interactions per magnetic ion per formula unit.

Using this formula and cation distribution determined from Neutron diffraction, the T_c values are calculated and they are listed in Table 2. The T_c values also obtained from ac-susceptibility method. From table, it is observed that there is difference in T_c's obtained from two methods and difference is large for ferrites with higher Ti content.

Non-collinear structure :

From the Table 1, it is observed that the A-site moment is close to the free ion value. The B-site moments on the other hand are smaller than their estimated free ion values, suggesting that the B-site moments are non collinear. The occurrence of localized canting has been reported in tetravalent and zinc mixed ferrites [9]. In treating our data with the

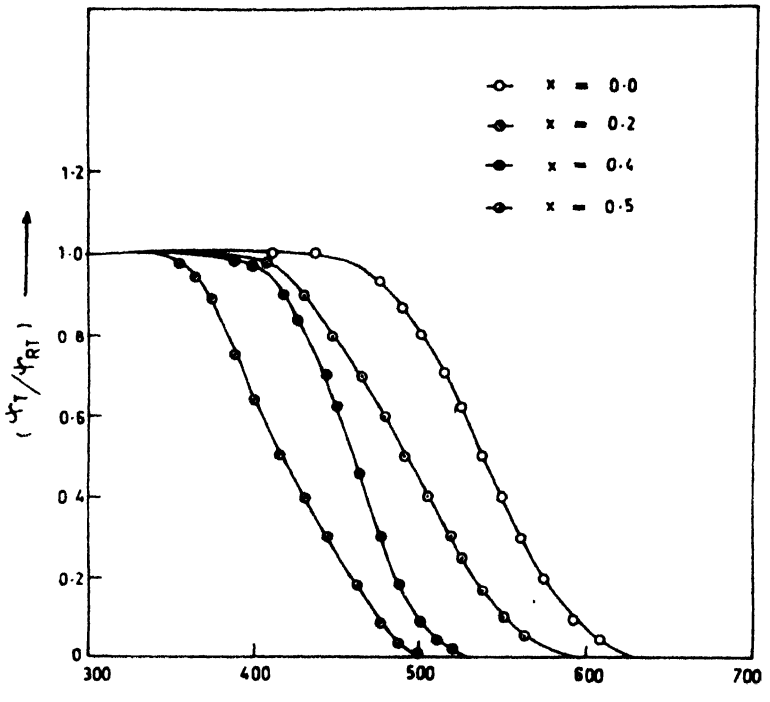

Figure 3. Variation of ac-susceptibility with temperature for $Ni_{0.5+x}Zn_{0.5}Ti_xFe_{2-2x}O_4$ system.

assumption of non-collinear structure at B-site. With a canting of Yafet-Kittel type on the B-site and spatial ordering of the transverse spin component of the magnetic moment should give rise to the (200) reflection, which is purely magnetic in nature. None of the systems studied here show this reflection. However, the absence of (200) does not rule out

the possibility of a canted structure as has been shown in many cubic spinels [10,11]. Such a behaviour can be explained on the basis of a long range ferrimagnetic ordering of the longitudinal component with the *A*-site moments, and a disordered normal component. The system under study, could have similar behaviour.

The temperature dependence of the normalized susceptibility for these samples are also been studied. The plots are shown in Figure 3. From the nature of these plots, it is observed that χ_{ac} remains almost constant in all the samples until the temperature reaches nearer to Curie temperature. χ_{ac} drops to zero at Curie temperature. However, tailing effect is observed for higher content of Ti. It is also noted that tailing in χ_{ac} curve near Curie temperature is due to canting in ferrites. Our samples show tailing effect. This observation support our conclusion of the presence of a canted ordering in these materials.

4. Conclusion

The neutron diffraction and magnetic measurements on the series of Ti substituted Ni–Zn ferrites show that the magnetic moment on the octahedral site is reduced and can be explained on the basis of a canted spin arrangement.

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